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(54) PHOTO-CURABLE COMPOSITE MATERIALS

(71) We, SUMITOMO CHEMICAL COMPANY LIMITED, a Japanese Body Corporate, of No. 15, Kitahama 5-chome, Higashi-ku, Osaka-shi, Osaka-fu, Japan do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

The present invention relates to photo-curable composite materials which are useful for preparing various stencils for screen printing, textile printing or the like.

Processes for forming patterns or images on photo-sensitive resin materials such as a photo-curable resin material by irradiation with actinic light have been previously studied and have already been utilized in the practical preparation of etching resists, reliefs and other printing materials such as stencils.

As the photosensitive resin materials used for preparing stencils, there have generally been used the so-called solvent-dry type sensitizing solutions prepared by dissolving a solid photo-crosslinkable resin in a solvent. However, when coating a solution of this type on a screen material, the solvent evaporates giving rise to unpleasant and toxic vapour in the working environment. In addition, when a thick coating layer of the resin is desired, it is highly desirable to build up the coating in layers, and a fairly long period of time is required for drying the coated product and exposing it to actinic light to form a pattern or image thereon. Therefore, improvements in such materials are badly needed.

On the other hand, photopolymerizable-crosslinkable resins have been commonly used as photosensitive resins for forming a relief. These resins are available in solid form as well as in liquid form. Some attempts have been made to prepare stencils by laminating a sheet made of this solid type resin to gauze. However, the printing material is expensive and plate-making takes a long time even though the solid photosensitive resin sheet can be easily handled and processed by an inexpensive plate-making machine. Moreover, other problems such as poor adhesion in laminating occur.

Liquid resins are an attractive alternative, because the printing material is inexpensive and plate-making is relatively rapid.

However, when a liquid resin is used in the preparation of a stencil, it is necessary to shape the resin into a layer having a pre-determined thickness and area before photo-setting it by irradiation with actinic light to form an image. In addition, when a liquid resin is shaped into a composite material together with gauze, it is necessary to handle the resin carefully since small air bubbles are liable to be included therein. This is time-consuming and requires special techniques. Furthermore, excess resin tends to become scattered about and the working environment is polluted. In addition, partially insufficient photo-setting occurs since a liquid resin is liable to form waves or otherwise move during the irradiation step, which disturbs the image to be formed thereon and results in partial lack of images, poor image reproducibility and poor resolution.

The invention provides a photo-curable composite, comprising a flexible film, the peripheral portion of which is bonded to, or continuous with a second flexible film to define a closed space between the two films, and a liquid, photo-curable resin composition and a liquid permeable screen material in the space between the two films, at least one of the films being capable of transmitting light of a frequency that will cause curing of the photo-curable resin.

The main component of the composite of the invention is a liquid photo-curable resin.

The composite may be used for preparing various stencils and requires no special plate-making machine.

A number of preferred embodiments of the invention will now be described with reference to the accompanying drawing, in which:-

Figure 1 is a schematic plan view of a preferred embodiment of a photo-curable composite according to the present invention;

Figure 2 is a schematic cross-section of the composite shown in Figure 1;

Figure 3 is a schematic cross-section of another preferred embodiment of a photo-curable composite according to the present invention; and

Figure 4 is a schematic cross-section of still another preferred embodiment of a photo-curable composite according to the present invention.

Stencils prepared using the composite of the present invention, may be used, for example in screen printing, textile printing or the like. In general, the composite comprises a, flexible and photo-transmitting thin film (A); a flexible film (B); a liquid photo-curable resin and a screen material, said films (A) and (B) being air-tightly bonded to each other at the peripheral portion thereof to form a flat inner space therein, said inner space being filled with said liquid resin to form a layer and said screen material being also placed in the inner space substantially parallel with the inner walls of the films (A) and (B).

In the composite material of the present invention, despite the use of a liquid resin, there is no need to shape a liquid resin into a specific layer before irradiation since it is enclosed in an air-tight manner in a package or bag formed with films (A) and (B) in the form of a layer having a pre-determined thickness and area when placed flat. Moreover, problems such as partial lack of images, poor image reproducibility or the like are eliminated since the formations of waves and the movement of the liquid resin during the image forming procedure is prevented by the package formed by films (A) and (B).

Referring now the drawings, Figures 1 and 2 show respectively a schematic plan view and section of a preferred embodiment of the photo-curable composite of the present invention. The composite material 1 comprises a, flexible and light-transmitting thin film (A) 2, a flexible film (B) 3, a liquid photo-curable resin 4 and a screen material 5. The films (A) and (B) are air-tightly bonded to each other at the peripheral portion 6 to form an inner space, that is, a package which is filled with the liquid resin 4 in a form of a layer. In the inner space, there is also placed the screen material 5 substantially parallel with inner walls of the films (A) and (B). Generally, the composite material 1 is prepared by bonding the films (A) and (B) at their peripheral portions in an air-tight manner to form a bag and putting therein the liquid resin 4 and the screen material 5 and then sealing the bag.

The film (A) used in the present invention should have light-transmitting properties and flexibility. It is sufficient that film (A) has enough light-transmitting properties to permit substantial transmission of actinic light through the film at a frequency suitable for curing the resin. Preferably, the transmittance of film (A) is 50% or more preferably 90% or more.

In use the image forming portion of the composite material of the present invention is placed flat on a flat surface or inserted between flat surfaces and held flat for irradiation by actinic light.

The flexibility of film (A) is required to prevent the composite material of the present invention from breakage by bending during handling.

Generally, the thickness of film (A) may be 5 to 100 microns. However, it is preferable to use a film 50 microns or less in thickness to minimize fogginess of the image produced since, for the formation of an image, a photo-mask is often placed on the outer surface of film (A), which may cause fogginess of the image. Furthermore, it is preferable that film (A) has a good peelability since it should be peeled off after photo-setting of the liquid resin to obtain a stencil. Examples of film (A) are regenerated cellulose; thermoplastic resins such as polyethylene, polypropylene, polyesters, polystyrene polyvinyl chloride and nylon; and laminated films of two or more thereof.

The film (B) should have flexibility. If desired, it may also have light-transmitting properties like film (A). The thickness of film (B) is not critical, but is preferably from 5 microns to 5 mm, more preferably from 10 microns to 1mm. Of course, a film having the same properties or characteristics as the above film (A) may be used as film (B). In this case, films (A) and (B) may be merely a sheet of a flexible and light-transmitting thin film as described above which is doubled to form a bag.

In some cases, it is preferable to previously treat the surface of the film by coating or finishing to provide improved adhesion and reflecting properties.

The liquid photo-curable resin used in the composite of the present invention is preferably a liquid composition having a viscosity of from 1 to 10^6 cp at room temperature and solidifying by photo-crosslinking, photopolymerizing or both when it is irradiated with so-called actinic light having a wave length of from 2,000 to 8,000 Å. Examples of such liquid compositions are those containing a photopolymerization initiator and a compound

which contains an addition-polymerizable ethylenically unsaturated bond. For example, those liquid photo-curable resins disclosed in United States Patent No. 2,760,863, French Patent Nos. 1,591,116 and 1,471,432 and Japanese Patent Publication (unexamined) No. 155303/1975 may be used. Also, commercially available liquid resin products for letterpress printing can be used as the liquid photo-curable resin in the present invention. Examples of these are APR (Trade Mark of a letterpress printing resin produced and sold by Asahi Chemical Industry Co.), Letter Flex (Trade Mark of letterpress printing resin produced and sold by W.R. Grace Co.), Revista (Trade Mark of letterpress printing resin produced and sold by Teijin Co.) or the like.

In the past, the viscosity of liquid resins used in plate-making has set limitations on the particular process and equipment to be used. In the present invention, however, there is no limitation on the viscosity of the liquid photo-curable resin used since the resin is packed in an air-tight flat package as described above. Thus, in the present invention, various liquid resins can be used, having any viscosity for example free-flowing liquid resins as well as highly viscous liquid resins.

The composition of the liquid resin used in the present invention will be properly determined by those skilled in the art according to the particular use of the stencil to be produced. Other solid ingredients such as pigments, fillers, reinforcing agents or the like may also be added to the liquid resin in amounts such that they do not affect the photo-curability of the resin.

The screen material, used in the present invention, is a sheet material through which liquid can preferably permeate freely. Suitable for example, are the so-called screen mesh for screen printing or textile printing, cloth or non-woven fabric, net, the so-called metal filter prepared by etching or plating metals or the like. They may be made of silk, polyesters, polypropylene, high-density polyethylene, nylon, glass, various metals or the like.

Although the thickness of the screen material depends upon the particular use of the stencil obtained from the composite material of the present invention, it is preferably equal to or less than the thickness of the photo-curable resin layer in the inner space formed with films (A) and (B). Preferably, the thickness of the screen material is from 20 microns to 1 mm. The mean size of opening or mesh of the screen material is 1 micron to 10 mm, preferably 10 microns to 5 mm.

In one embodiment of the present invention, the liquid resin in the inner space is partially impregnated in the screen material, the remaining liquid resin is located between the screen material and film (A) or (B) as shown in Figure 2. In another embodiment, the liquid resin in the inner space may almost be impregnated in the screen material and thereby the screen material may be substantially contiguous to or in contact with the films (A) and (B) as shown in Figure 3.

As described above, the bag formed by the films A and B is filled with the liquid photo-curable resin and the screen material and air-tightly sealed.

For enclosing the resin and the screen material, films (A) and (B) are bonded to each other. It is convenient to employ a known melt-bonding process, heat-bonding process or photo-bonding process for this purpose. However, a suitable adhesive may also be used if these processes are difficult to employ. It is desirable to use films selected from the group consisting of thermoplastic resin thin films and laminates thereof as films (A) and (B) since they can be readily melted and bonded to each other by heating to give an air-tight seal and there is no trouble such as leakage of the enclosed liquid resin on handling. Preferably, the sealing is carried out while preventing inclusion of any air bubbles into the bag.

For example, the photo-curable composite material of the present invention is prepared by the following several processes:

(1) The composite material is prepared by placing a flat screen material on film (B), coating a liquid photo-curable resin thereon, further placing film (A) thereon and then sealing the composite at the peripheral portion thereof;

(2) The composite material is prepared by forming a flat bag with films (A) and (B), putting a flat screen material and a liquid resin into the bag, and then sealing the bag; or

(3) The composite material is prepared by a continuous process in which a flat screen material and a liquid resin is put into a bag while the bag is continuously formed with rolled sheet product(s) of film (A) or films (A) and (B) and then the bag is sealed.

Any of these processes can be automatically carried out by a technique known to the prior art so as to produce the composite materials of the present invention at a low cost in mass production.

The required volume of the liquid photo-curable resin to be enclosed in the composite material of the present invention is dependent upon the desired thickness and area of the stencil to be produced and determined by the particular volume of the inner space formed with films (A) and (B). The mean thickness (calculated value) of the photo-curable resin

layer in the inner space is determined taking into consideration the photo-setting properties of the resin used such as the photo-setting rate, strength of the cured resin or the like. The thickness of the resin layer may be 10 microns to 10 mm, preferably 0.05 to 5 mm. When colored products are desired, the mean thickness is preferably 0.05 to 1 mm since the photo-setting thereof is not facile in comparison with an uncolored product.

Usually the screen material is wholly enclosed in the inner space formed with films (A) and (B) and placed parallel with inner walls of the central part of films (A) and (B). However, the peripheral ends of the screen material may protrude out of the inner space between films (A) and (B) without breaking the air-tightness of the inner space. In this case, it is very convenient to handle the composite material since the screen material is fixed between films (A) and (B).

To prepare a stencil from the photo-curable composite material of the present invention, the material is treated, for example, as described hereinafter.

(1) Firstly, the composite material of the present invention is placed on a flat plate (e.g. glass plate) with the film (A) side turned upward.

(2) Then, one or more spacers having the desired thickness are placed around the peripheral portion of the composite material.

(3) A photo-mask is placed on the composite material while preventing the film (A) from wrinkling.

(4) Further, a light-transmitting plate having good flatness and capable of transmitting radiation of a frequency suitable for curing the polymer (e.g. glass plate, quartz plate or the like) is placed on the above assembly to cover all the top surface thereof and pressed downwardly until the light-transmitting plate is contacted with the spacer(s) and thereby the photo-mask is brought into an intimate contact with the surface of film (A). When the thickness of the spacer used is not a suitable one, the following operation may be carried out:

Where the thickness of the spacer is too large and the volume of the liquid resin is too small to intimately contact the light-transmitting plate with the photo-mask over the whole image area, one or more pieces of supplemental soft sheet materials are inserted between the plate and the upper film at suitable portions where no image is formed, e.g. around the edges to drive liquid into the image forming areas.

On the other hand, where the thickness of the spacer is too small and the volume of the resin is too large to contact the light-transmitting plate with the spacer, the light-transmitting plate is moved closer so as to drive the enclosed excess resin aside from the image area.

(5) After completion of intimate contact of the light-transmitting plate with the assembly, the resin is cured by irradiation with actinic light through the light-transmitting plate, the photo-mask and film (A) to form images or patterns thereon.

(6) The composite material is taken out, and film (A) or film (B) or both films (A) and (B) are peeled off therefrom, followed by development of the image by removing the uncured resin. The removal of the uncured resin can be carried out according to the nature of the resin used by a method known to the prior art such as wiping-off, suction, blowing-off, rubbing-off, washing-out with detergent or an organic solvent or the like.

(7) And then, drying and post-irradiation are carried out, if necessary, to obtain the desired stencil.

It has now been found that the composite material of the present invention becomes more convenient for use by integrating a spacer which has a pre-determined thickness in the inner space adjacent to the bonded portion of films (A) and (B). The thickness of the spacer is properly determined in consideration of the volume of the resin filled in the inner space. When using the composite material of this type, the image forming step becomes more simple and the above procedure (2) can be omitted. Further, the above procedure (4) can be carried out more surely, simply and rapidly.

Turning to the accompanying Figure 4, there is shown a schematic section of another preferred embodiment of the composite material having a integrated spacer in the inner space.

Like the composite material 1 shown in Figure 1 and 2, the composite material 1' as shown in Figure 4 also comprises a film (A) 2, film (B) 3, a liquid photo-curable resin 4 and a screen material 5. Further, the composite material 1' has a spacer 7 in the inner space adjacent to the bonded portion 6.

The material and shape of the spacer are not critical. The length, width, shape and number of the spacers may be determined so as not to deform the spacer under the pressure when contacting the photo-transmitting plate with the assembly in the image forming step. It is preferable to use a tape made of a solid flexible resin which is capable of melt-bonding or bonding as the spacer since it can be integrated more easily. In practice, two flat tape spacers are arranged at both side ends of the inner space, or a frame of tape spacers is

arranged around the inner space adjacent to the bonded portion. This is convenient for use in practice.

Further, when a screen material has enough thickness to impregnate all the liquid resin layer in the inner space in its own structure (see Figure 3), the screen material per se acts as a spacer and therefore the resin is readily cured in a definite thickness.

Thus, the composite material of the present invention has following advantages.

(1) The material causes no leakage of a liquid resin and pollution of the working environment and is convenient for use since the liquid resin is air-tightly enclosed in a light-transmitting package.

(2) There is no influence of oxygen and therefore even resins such as those which are easily hindered from curing by oxygen can be used without any problem since the liquid resin is air-tightly enclosed in a package.

(3) The viscosity of liquid photo-curable resins can be varied widely and the change of viscosity according to the change of temperature does not affect the image formation.

(4) Adjustment of the thickness of the composite material before image formation can be carried out very simply without requiring any expensive equipment.

(5) Image reproducibility and image resolution of the product prepared from the composition material are superior to those of any conventional image forming process since waving or movement of the liquid resin is inhibited in the image forming step and no disturbance and lack of images are observed.

(6) The thickness of the liquid resin layer can be easily adjusted on the spot.

(7) The composite material is inexpensive since the liquid photo-curable resin is used as a main component and it does not take a long time in image forming.

(8) When only a part of the composite material has been irradiated, the remaining non-irradiated part can be saved for later use by cutting off the irradiated part along a line where the irradiation has solidified the polymer so as to seal of the liquid resin in the remaining non-irradiated part.

Further, since the flat screen material is also enclosed in the inner space of the composite material, there exists some other advantages as follows.

(9) The patterns formed with the cured resin do not break up into pieces and are linked to each other, even when both films (A) and (B) are peeled off after image formation.

(10) In case of coating a liquid photo-curable resin on a screen, small air bubbles are liable to be included therein unless the operation is carried out carefully. When using the composite material of the present invention, there is no need for such an operation and it is possible to start the irradiation step immediately.

Thus, according to the present invention, various stencils having high-quality photo-cured images can be obtained at a low cost. That is, the composite materials of the present invention can be used for the preparation of various stencils for providing various patterns including screen printing and textile printing. They are also used for the preparation of hollow letters, hollow patterns or the like.

The following examples illustrate the present invention but are not to be construed as limiting the scope thereof.

Examples 1 to 6

The composite materials listed in the following Table 1 were prepared and their properties were evaluated as follows:

Six bags, each having an effective inner space area of 210 mm × 250 mm were made of the light-transmitting thin films (A) and the films (B) listed in Table 1, respectively. The screen listed in Table 1 having an appropriate size and the required amount of a liquid photo-curable unsaturated polyester type resin (viscosity: 1100 cp at 25°C) were put into each of the above prepared bags and spread out in a uniform thickness. Each bag was then sealed by heating while preventing infiltration of air to obtain the desired composite material.

Each composite material thus obtained was placed on a flat working stand with the film (A) side turned upward and a steel belt spacer arranged adjacent to both of the side ends of the material. A photo-mask was placed on the surface of the material and then a float glass plate of 200 mm × 240 mm × 10 mm (thickness) was placed thereon. After smoothing wrinkles on the surface of the composite material, the assembly was irradiated through the glass plate with ultraviolet fluorescent lamps (20 W × 5), 10 cm apart from the glass plate, for 2 minutes. When the irradiation was completed, the composite material was taken out, cut open at one end thereof and one of the thin films was peeled off. This was then developed with an aqueous weak alkaline solution and dried to give the desired stencil product which was evaluated as to its image reproducibility (Image), image resolution and thickness accuracy. The results are shown in Table 1.

TABLE 1

Example no.	Photo-curable composite material				Thickness of spacer	Evaluation of photo-cured product		
	Light-transmitting thin film (A)	Film (B)	Amount of resin	Screen		Image	Resolution	Thickness accuracy
1	Polyethylene (38 μ)*	Polyethylene (38 μ)*	5 g	Polyester gauze 300 mesh (100μ)*	0.1 mm	Good	150 μ	± 0.01 mm
2	Polypropylene (20 μ)	Polypropylene (45 μ)	5 g	Silk gauze 200 mesh (70 μ)	0.01 mm	Good	200 μ	± 0.01 mm
3	Polyethylene/ nylon laminate (35 μ)	Polyethylene/ nylon laminate (35 μ)	10 g	Glass mat (80 μ)	0.2 mm	Good	200 μ	± 0.02 mm
4	Polyethylene (38 μ)	Polyethylene (38 μ)	12 g	Polyester gauze 60 mesh (100 μ)	0.2 mm	Good	200 μ	± 0.01 mm
5	Polyethylene/ nylon laminate (35 μ)	Polyethylene/ nylon laminate (80 μ)	10 g	SUS mesh** 200 mesh (100 μ)	0.2 mm	Good	200 μ	± 0.01 mm
6	Polyethylene (38 μ)	Polyethylene/ nylon laminate (80 μ)	25 g	Nylon gauze 60 mesh (200 μ)	0.5 mm	Good	250 μ	± 0.05 mm

[Note]: * - Thickness ** - Stainless steel

Example 7

According to the similar procedure as described in Example 1, a composite material was prepared by adhering two spacers made of hard paper of 200 mm × 20 mm × 0.2 mm (thickness at opposite side ends of the inner space of a bag formed with the same films as in Example 3. This bag was filled with a polyester gauze (200 mesh, thickness 100 microns) and 8 g of the liquid photo-curable unsaturated polyester resin and then heat-sealed while preventing infiltration of air to give a desired composite material. Similar to Examples 1 to 6, the image formation was carried out on the composite material but without using any special spacer. Thus, a high-quality stencil having thickness accuracy of ± 0.01 mm was obtained.

Example 8

A polyester film having 12 microns of thickness was placed on a flat glass plate and then a 100-mesh polyester gauze having 110 microns of thickness was placed thereon. A liquid unsaturated polyester type resin was coated on the gauze and then polyester film having 12 microns of thickness was placed on the coated surface. A float glass plate was placed on the laminate and pressure was applied thereto.

After covering the central portion of the glass plate with masking film, the peripheral portion thereof was exposed to actinic light to cure the resin and two sheets of the films and the gauze were bonded together. Image formation was carried out in the same manner as in Example 7, and a high-quality stencil having thickness accuracy of ± 0.01 mm was obtained.

WHAT WE CLAIM IS:-

1. A photo-curable composite, comprising a flexible film, the peripheral portion of which is bonded to, or continuous with a second flexible film to define a closed space between the two films, and a liquid, photo-curable resin composition and a liquid permeable screen material in the space between the two films, at least one of the films being capable of transmitting light of a frequency that will cause curing of the photo-curable resin.

2. A composite as claimed in claim 1 including a spacer in the closed space adjacent to the peripheral portion of the films, to space the films apart.

3. A composite as claimed in claim 1 or claim 2, wherein the amount of the liquid resin in the space is such that it forms a layer from 10 microns to 10 mm thick when the composite is put on a level surface.

4. A composite as claimed in claim 3, wherein the amount of the liquid resin is such that it forms a layer from 50 microns to 5 mm thick, when the composite is put on a level surface.

5. A composite as claimed in any one of claims 1 to 4, wherein the thickness of the or each light transmitting film is from 5 to 100 microns.

6. A composite as claimed in any one of claims 1 to 5, wherein the or each light transmitting film is a polyethylene, polypropylene, polyester, polystyrene, polyvinyl chloride, nylon, or regenerated cellulose film.

7. A composite as claimed in any one of claims 1 to 6, wherein at least one of the films has an optical transmittance of 90% or more at frequencies causing curing of the photo-curable film.

8. A composite as claimed in any one of claims 1 to 7, wherein the films are of the same material.

9. A composite as claimed in any one of claims 1 to 8, wherein the screen material is a screen mesh, cloth, non-woven fabric, net or metal filter.

10. A composite as claimed in any one of claims 1 to 9, wherein the thickness of said screen material is from 20 microns to 1 mm.

11. A photo-curable composite substantially as hereinbefore described with reference to, and as shown in the accompanying drawings.

12. A photo-curable composite substantially as hereinbefore described in any one of Examples 1 to 8.

13. A method of preparing a composite as claimed in any one of the preceding claims, which comprises sealing a liquid, photo-curable resin composition and a screen material between the films as defined in claim 1.

14. A method of forming a stencil, which comprises image-wise exposing a composite as claimed in any one of claims 1 to 12 with actinic light through a or the said light transmitting film to cure the resin and developing the exposed composite.

15. A stencil, when formed by a method as claimed in claim 14.

16. A stencil as claimed in claim 15, when used as a stencil.

17. A method of printing, which involves the use of a stencil as claimed in claim 15 or claim 16.

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1589559 COMPLETE SPECIFICATION

1 SHEET

This drawing is a reproduction of the Original on a reduced scale

FIG. 1.

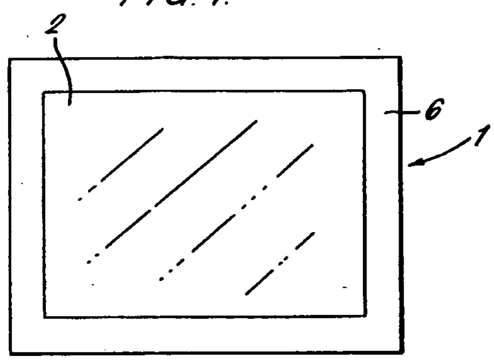

FIG. 2.

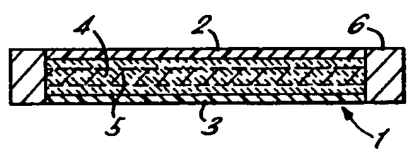

FIG. 3.

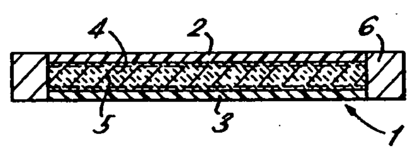

FIG. 4.